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A BASIC STUDY OF VACUUM-FUSION ANALYSIS OF REFRACTORY METALS FOR GASES

By

M. W. Mallett, D. F. Kohler, R. B. Iden, and B. G. Koehl
Battelle Memorial Institute
505 King Avenue
Columbus 1, Ohio

May 1962

Final Report
Contract No. DA-33-019-505-ORD-11
Cleveland Ordnance District
OCO, R&D Branch Project TB4-004
Department of the Army Project 5B93-32-004
Watertown Arsenal
Watertown 72, Mass.

TECHNICAL REPORT WAL TR 823/5

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ABSTRACT

Various techniques for determination of oxygen in the refractory metals columbium, tantalum, molybdenum, and tungsten by the vacuum-fusion method were evaluated. The platinum bath at 1900 C and a Pt:M ratio as low as 1:1 is satisfactory for columbium and tantalum. An iron bath at 1650 C and a maximum molybdenum or tungsten content of 30 per cent is recommended for molybdenum and tungsten. Hydrogen absorption by a Hopcalite-Ascarite mixture was shown. This leads to some error in oxygen analyses made with this absorbent. The use of a gas chromatograph and internal gas standard for analysis of vacuum-fusion gases was demonstrated.

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INTRODUCTION

The vacuum-fusion method is the principal and most reliable means of determining gases in metals. Achieving its successful application to the refractory metals columbium, tantalum, molybdenum, and tungsten is of current interest. Studies with this goal were recommended by the MAB Panel on Analytical Problems in Refractory Metals as covered by Report MAB-154-M-(1), Volume II — Panel Reports, Chapter III. In addition to the need to evaluate and improve the analytical procedures per se there is a need for a critical study of design of apparatus components such as furnace, pumps, gages, connecting tubing and volumes, catalyst tubes and freezing traps. Moreover, the performance of oxidizing catalysts and gas adsorbents needs investigation for efficiency, selectivity, and contribution to blank gases. Such studies could lead to minimizing blanks, one of the main deterrents to precise and accurate analyses in the range of 1 to 10 ppm oxygen. They would also reveal whether side reactions of catalysts and adsorbents are preventing exact quantitative fractionation of the extracted gases.

With these goals in mind, a research program was set up which included some items for which immediate conclusions could be reached and others which might require continued effort over several years. The results of the study are conveniently grouped as pertaining either to analytical techniques or apparatus design.

SUMMARY

The performance of several vacuum-fusion techniques for determination of oxygen was evaluated in application to the refractory metals columbium, tantalum, molybdenum, and tungsten.

Columbium

Use of the platinum bath at 1900 C with 1.5-g samples and an extraction time of 30 min is recommended. The Pt:Cb ratio may be as low as 1:1 for the final sample.

The technique of diffusion extraction at 2000 C for 30 min gave results which ranged from perfect agreement to 4 per cent lower than those by the platinum bath.

The platinum-flux technique is unsatisfactory because of the high oxygen content of the platinum.

A limited study of accuracy of the oxygen analysis for columbium was inconclusive because of the difficulty of obtaining low-oxygen metal.

Tantalum

The platinum-bath technique gave excellent results for oxygen in tantalum under the same conditions recommended for columbium.

Diffusion extraction at 2000 C for 30 min gave very reproducible results but they averaged about 10 per cent lower than those obtained by vacuum fusion.

Oxygen-doping experiments with the analysis made by diffusion extraction gave results about 10 per cent lower than the nominal oxygen content. Further experiments with analysis by platinum bath are recommended.

Molybdenum

Analysis of molybdenum by the iron-bath technique at 1650 C and a 20-min extraction gave good reproducibility at the 3-ppm oxygen level. A platinum-bath technique for molybdenum appeared unsatisfactory. Extraction at 2000 C for 30 min with a Pt:Mo ratio of 30:1 to 10:1 gave results slightly higher than those obtained with the iron bath.

Tungsten

Oxygen analysis of tungsten with an iron bath at 1650 C for 20 to 30 min and a maximum tungsten concentration of 30 per cent appeared satisfactory for 2-g samples. Samples weighing 0.2 g gave erratic results. Analyses with a platinum bath at 2000 C for 20 min were erratic. Even with a Pt:W ratio of 10:1 samples were incompletely dissolved. Reproducible results were obtained at 1900 C but it is believed the same results could be obtained by diffusion extraction in the absence of the bath.

Hopcalite-Ascarite Absorbent

The rapid and complete absorption of CO in 3 to 5 min at room temperature was confirmed. However, it was demonstrated that this absorbent also gave a slow and continuous hydrogen absorption. This effect, under certain circumstances, could lead to serious error in oxygen analyses.

Gas Chromatography of Vacuum-Fusion Gases

The applicability of a dual-column, dual-detector gas chromatograph to the analysis of gases extracted by vacuum fusion was demonstrated. Methane was used as an internal standard. A direct comparison was made of analysis by the gas chromatograph and low-pressure fractional freezing.

EVALUATION OF ANALYTICAL TECHNIQUES

EXPERIMENTAL PROCEDURES

Materials

An effort was made to obtain several hundred grams each of columbium, tantalum, molybdenum, and tungsten. These metals were to contain <100 ppm oxygen which was to be in homogeneous distribution. As it turned out 1/2-in.-diameter bar stock of both columbium and tantalum was obtained from Wah Chang Corporation. The manufacturer reported that the metal was prepared from presintered, powder metal bars double arc melted in a consumable-electrode vacuum arc furnace to 5-in.-diameter ingots. Ingots were scalped, cropped, and ultrasonically tested, then cold forged to 1-1/2-in. diameter and machine conditioned. The forging was cold swaged to oversize and centerless ground to size. The greatest impurity in the columbium (Battelle Lot B) was reported as <500 ppm for both tantalum and zirconium and <200 ppm tungsten. The tantalum contained <200 ppm tungsten and <100 ppm of each of several other elements. Oxygen was reported at <50 ppm (top) to 120 ppm (bottom) in the columbium ingots and <50 ppm (top and bottom) in the tantalum. Battelle analyses showed these values to be much too low.

A similar lot of columbium (Battelle Lot A) from the same source was found in stock in the Battelle laboratory. This contained about 40 ppm oxygen.

A small lot of 50-mil tantalum sheet containing about 7 ppm oxygen was also found in stock.

Efforts to obtain other tantalum and columbium samples containing <10 ppm oxygen were unsuccessful. One company informed us that their "equipment is not refined enough to produce this low a level of interstitial". Also, six 1/4 x 1-3/4-in. slices of electron beam-melted tantalum reported by the supplier, another company, to contain 13 ppm oxygen analyzed 51 to 138 ppm. This material was returned for credit.

The 1/4-in.-diameter molybdenum wrought bar (0.02 per cent carbon) was purchased from the Climax Molybdenum Company of Michigan.

Two 1/8-in.-diameter by 6-in.-long zone-purified tungsten rods were supplied by Mr. Judson Graab of NASA.

Platinum for baths consisted of 50-mil wire analyzing about 20 ppm oxygen and No. 4 gage wire analyzing 11 ppm oxygen.

Methods and Techniques

The methods and techniques investigated are given for the individual metals as reported under "Experimental Results". At the start of this study the known methods

were essentially those described by Mallett⁽¹⁾. Several phase diagrams pertinent to the various vacuum-fusion bath compositions are given in the Appendix.

EXPERIMENTAL RESULTS

Columbium

Platinum-Flux Technique

A number of experimental oxygen analyses were made on some high-purity, double arc-melted columbium rod from the Wah Chang Corporation. This material was designated by Battelle as Lot A. Several determinations were made by a platinum-flux technique with a Pt:Cb ratio of 7:1, and a 30-min extraction at 1900 C. The platinum flux in the form of 50-mil wire was wound tightly around the sample. This technique has been highly successful for titanium.⁽²⁾ Results for 1-g samples ranged from 20 to 120 ppm oxygen. About 50 ppm of the discrepancy was due to apparent variation in the oxygen content of the 50-mil platinum-wire flux. In some cases the total oxygen blanks from platinum were as high as 150 ppm. Furnace blanks were equal to only 10 to 15 ppm oxygen. Because of the large blanks and variations therein it was decided that application of the flux technique to columbium was not practical, particularly for oxygen contents below 100 ppm.

It will be shown later that the advantages of dissolving columbium samples in platinum are better obtained with the platinum in the form of a bath which can be degassed before dropping samples.

Platinum-Bath Technique

The 6-ft length of 1/2-in.-diameter high-purity, double arc-melted columbium rod purchased from Wah Chang Corporation (Lot B) was spot checked for homogeneity of oxygen content. Eight samples from positions scattered throughout the length of the rod yielded values of 121 to 157 ppm by diffusion extraction at 2000 C. Adjoining samples tended to give duplicate results. Hydrogen was quite uniform, ranging from 6 to 8 ppm. Nitrogen ranged from 24 to 37 ppm and was not necessarily a function of position of sample in the rod.

Eight other Lot B columbium samples from consecutive positions in the rod were analyzed by the platinum-bath technique at 1900 C for 30 min. The samples weighed 1.5 g each and the Pt:Cb ratio was 4:1. Oxygen averaged 163 ppm with a standard deviation of 5.3 ppm and a coefficient of variation of 3.3 per cent. This demonstrates the good reproducibility of results by this analytical technique. The individual results in the order obtained are given in Table I.

(1) M. W. Mallett, Talanta, **9**, 133-144 (1962).

(2) W. R. Hansen, M. W. Mallett, and M. J. Trzeciak, Analytical Chemistry, **31**, 1237 (1959).

TABLE 1. OXYGEN IN COLUMBIUM USING
A BATH OF Pt:Cb = 4:1

Oxygen, ppm	(X - \bar{X})	(X - \bar{X}) ²
168 ± 4 ^(a)	5	25
154	-9	81
165	2	4
161	-2	4
168	5	25
159	-4	16
169	6	36
$\bar{X} = \frac{161}{10} = 16.1$	$\frac{-2}{10} = -0.2$	$\frac{4}{10} = 0.4$
$\bar{X} = 163$	$\Sigma = 1$	$\Sigma = 195$

Note: Standard deviation = 5.3 ppm
Coefficient of variation = 3.3 per cent.
(a) Precision of measurement.

In the interest of finding a means of conserving platinum, a further series of analyses was made with a platinum bath with Pt:Cb = 1:1 by weight. Platinum additions were made before dropping each sample so that the exact 1:1 ratio existed for each analysis. Extractions were made with 1.5-g samples of Lot B columbium at 1900 C for 20 min with consecutive results as given in Table 2.

TABLE 2. OXYGEN IN COLUMBIUM USING
A BATH OF Pt:Cb = 1:1

Sample	Oxygen, ppm	Sample	Oxygen, ppm
1	169	7	150
2	165	8	165
3	166	7	168
4	163	10	152
5	169	11	171
6	153	12	155

Note: Average = 162 ppm
Standard deviation = 7.5 ppm
Coefficient of variation = 4.6 per cent.

It is seen that these results compare very favorably with those obtained where the minimum ratio of Pt:Cb = 4:1. Since the 1:1 weight ratio becomes on a volume basis, Pt:Cb = 0.4:1 it is not advisable to reduce the ratio further. Our latest turnaround cost for platinum is \$0.63 per gram. On this basis, the platinum cost per sample is \$0.95 which is certainly very reasonable.

Diffusion-Extraction Technique

Eight other samples of Lot B columbium from the same section of the rod as analyzed by the platinum-bath technique were analyzed by diffusion extraction⁽³⁾ at 2000 C for 30 min. Oxygen averaged 157 ppm with a standard deviation of 2.0 ppm and a coefficient of variation of 1.3 per cent as shown in Table 3. It is seen that the reproducibility of results by this method is excellent. However, the average result is lower than the platinum-bath average by 6 ppm or 3.7 relative per cent. A similar discrepancy of about 10 relative per cent was noted for tantalum analyzed by the two methods as will be shown later. Since the same bias was found for the oxygen-doping experiments, (to be described later), it must be concluded that some oxygen is unaccounted for by the diffusion-extraction technique. This is consistent with reports of volatile suboxides produced by columbium and tantalum. It appears that at least a portion of these suboxides is not converted to CO during diffusion extraction. For routine analyses or detecting changes in composition at the >100-ppm level, this discrepancy is not important. However, where absolute values are required as in the doping experiments, it appears that the diffusion-extraction technique cannot be used.

TABLE 3. OXYGEN IN COLUMBIUM BY
DIFFUSION EXTRACTION

Oxygen, ppm	$(X - \bar{X})$	$(X - \bar{X})^2$
159 ± 4	2	4
157	0	0
159	2	4
159	2	4
153	-4	16
156	-1	1
157	0	0
157	0	0
$\bar{X} = 157$	$\Sigma = 1$	$\Sigma = 29$

Note: Standard deviation = 2.0 ppm

Coefficient of variation = 1.3 per cent.

In a further comparison of the platinum-bath and diffusion-extraction methods six samples of Lot A columbium were analyzed at 1900 C for 30 min in a platinum bath (Pt:Cb = 4:1) of melted and degassed wire. Analyses ranged from 44 to 48 ppm oxygen with an average of 46.3 and a standard deviation of 1.6.

A set of five similar samples analyzed by diffusion extraction at 2000 C for 30 min yielded 44 to 49 ppm oxygen for an average of 46.8 and a standard deviation of 2.2. Thus, good agreement between the platinum-bath and diffusion-extraction methods is demonstrated. The methods show coefficients of variation of 3.5 and 4.7 per cent, respectively, which indicate satisfactory reproducibility of both. In this case the bias toward lower values by diffusion extraction was not found.

(3) W. R. Hansen and M. W. Mallett, Analytical Chemistry, 29, 1868-1869 (1957).

Iron-Bath Technique

The platinum-bath technique for the analysis of columbium for oxygen has been discussed. If the ratio of platinum weight to sample weight is 4:1 and a 3.5-g sample is used (for a precision of ± 2 ppm) the cost of the platinum would be \$8.82 per sample. This is based on a turnaround cost for platinum of \$0.63 per gram. In view of this cost it seemed well to evaluate the iron-bath and iron-tin bath techniques reported in the literature. The results obtained on Lot B columbium with a nominal oxygen content of 163 ppm were as follows in Table 4.

TABLE 4. OXYGEN IN COLUMBIUM BY IRON
AND IRON-TIN BATHS

Columbium Sample	Bath		Oxygen, ppm
	Composition	Temperature, C	
1	67% pig iron - 33% vacuum- melted iron	1650	4
2	Ditto	1650	4
3	50% pig iron - 50% vacuum- melted iron	1850	200
4	50% pig iron - 50% vacuum- melted iron	1850	43
5	94% vacuum- melted iron - 6% Baker's tin	1650	140
6	Ditto	1650	66

Samples 1 and 2 apparently did not mix with the molten iron but lodged above the melt suspended by a large gas bubble on the surface of the bath. The Sample 3 analysis of 200 ppm hydrogen includes that of an additional piece of iron which it was necessary to drop in order to produce melting of sample. Improper mixing of sample and bath similar to that of Samples 1 and 2 resulted in the low figure for Sample 4. Sample 5 did not melt until additional tin was dropped on top of sample, then after 1 hr of gas collection the blank rate of the system had not yet been reached. Gas from Sample 6 was collected for 30 min then analyzed.

Two additional analyses of Lot B columbium were made using the iron-tin bath (94 per cent vacuum-melted iron — 6 per cent Baker's tin) at 1650 C with a minimum of 20-min extraction. The results, 114 and 101 ppm oxygen, were quite low.

Three more samples were analyzed by the iron-bath method at 1850 C for 20 min. Despite the use of tin additions before each sample the consecutive results were 148,

138, and 108 ppm oxygen compared with the nominal 163 ppm. Although the iron-bath experiments were few, there is no justification of further study of this technique. Certainly the low-cost, trouble-free platinum bath demonstrated in this study obviates the need for a different bath technique.

Analysis of Columbium Shot

In a preliminary report of results of the ASTM Columbium Task Force, Sub-Group on Oxygen in Columbium, Battelle's initial results on samples of D3A and D3B columbium shot (about 1/32 inch) were somewhat higher than the group average. In addition, the D3A shot showed particularly high deviations. For sets of five samples each, D3A showed an average of 102 ppm oxygen with a standard deviation of 21.5 and coefficient of variation of 21.1 per cent; D3B showed an average of 172 with a standard deviation of 12.4 and coefficient of variation of 7.2 per cent. Group averages for D3A and D3B were 62 and 142 ppm, respectively, by the platinum-bath technique. Since there was a great disparity between the poor agreement among these results and the good agreement among results obtained on project (WAL) columbium, it was deemed of value to study further the analytical behavior of the columbium shot.

The analysis of shot differed from the conventional analysis in that removal of surface films was not possible and incapsulation (in tin) of the sample was necessary for handling the sample. In the present analyses care was taken to minimize the weight of the tin wrapper. The almost perfect agreement of Battelle's platinum-bath results with the ASTM results is shown in Table 5. Battelle's average analysis for Sample D3A was 63 compared with the ASTM 62 ppm oxygen, and analysis for Sample D3B was identical with the ASTM 142 ppm. Also, the consistency of the results is excellent.

TABLE 5. OXYGEN IN ASTM COLUMBIUM SHOT

Analysis	Oxygen, ppm		Coefficient of Variation, per cent
	Average (a)	Standard Deviation	
<u>Sample D3A</u>			
Diffusion extraction, 2000 C	76	7.5	9.9
Platinum bath, 1900 C	63	2.3	3.7
ASTM Group	62	--	--
<u>Sample D3B</u>			
Diffusion extraction, 2000 C	145	3.9	2.7
Platinum bath, 1900 C	142	1.6	1.1
ASTM Group	142	--	--

(a) for five samples in each case.

Diffusion-extraction analyses of Sample D3B at 145 ppm agree well with the 142 ppm by the platinum-bath technique. However, for Sample D3A the diffusion-extraction result of 76 ppm is high compared with the 62 or 63 ppm by the platinum bath. The results also show more variation. No ASTM diffusion-extraction values are available for comparison except those of the Du Pont Experimental Station which reports 72 ppm.

The earlier discrepancies in Battelle results are now believed to have been due largely to variations in oxygen content of the tin-foil sample wrapper as later demonstrated by several analyses of random samples from the tin-foil stock. Interference from this source becomes practically negligible (at columbium oxygen levels of 50 ppm and higher) if a minimum uniform weight of tin is used in each case. Also, tin is believed to be a possible cause of higher results for columbium shot by diffusion extraction. That is, during its rapid evaporation from the crucible it may bombard cooler parts of the crucible and furnace walls releasing adsorbed oxygen.

One other possible cause of high and erratic oxygen analyses of columbium shot was investigated. Since it is routine to rinse certain samples in acetone there was some question as to whether the ASTM columbium shot had been rinsed. To check this, shot from the vial of D3A shot yielding erratic results was carefully analyzed without a rinse. Two samples gave 81 ± 1 ppm oxygen by diffusion extraction at 2000 C or essentially the same as some of the results included in the average of 76 ppm reported in Table 5. Two samples of the latter material rinsed in reagent-grade acetone analyzed 87 ppm each. This showed that there is a strong probability that the acetone rinse added about 10 ppm oxygen to these samples.

Oxygen-Doping Experiments

In view of the very satisfactory reproducibility of oxygen analyses of columbium by the platinum-bath technique, an attempt was made to determine the accuracy of the analyses by making measured additions of oxygen (doping) to oxygen-free or low-oxygen columbium. To obtain low-oxygen columbium it was decided to reduce the oxygen content of the Lot B columbium. This was done by electron-beam melting in the following manner. Four 10-g charges were placed in depressions in a water-cooled copper-slab crucible. Each charge was melted, increasing the electron-beam power within the limit of the supply until the system pressure decreased to about 3×10^{-5} mm of mercury. Each 10-g charge was remelted four times inverting the charge between melts. Pairs of charges were then consolidated into two 20-g buttons and inverted once and remelted. Considerable outgassing was noted during the initial melting of the 10-g charges.

Two samples from each 20-g button were then analyzed by diffusion extraction at 2000 C. One button gave 22 and 23 and the other 7 and 8 ppm oxygen. Hydrogen was at 1 and nitrogen at 7 ppm, both close to their limits of detection.

The remainders of the buttons were doped with 30 ppm oxygen in a micro-Sieverts apparatus to produce nominal compositions of 37, 53, and 54 ppm. Analysis showed 46, 62, and 63 ppm, respectively. The consistent discrepancy of +9 ppm oxygen appeared to be incidental to the micro-Sieverts processing. The limited supply of low-oxygen columbium precluded carrying a blank sample through the process. A less expensive source of low-oxygen (<20 ppm) columbium was sought. Inquiries to manufacturers indicated that such metal is not presently being produced commercially.

Tantalum

Platinum-Bath Technique

A series of eight 2-g tantalum samples from consecutive positions in the rod (Wah Chang) was analyzed by the platinum-bath technique with a Pt:Ta ratio of 4:1 at 1900 C for 30 min. Table 6 shows that oxygen averaged 103 ppm with a standard deviation of 2.8 and a coefficient of variation of 2.7 per cent. It was also observed that hydrogen values were quite consistent at 4 ppm which agrees within the limits of experimental error with the diffusion-extraction result of 3 ppm. Nitrogen values averaged 48 with a standard deviation of 4.9 ppm and a coefficient of variation of 10.3 per cent. The platinum-bath nitrogen is roughly four times that obtained later by diffusion extraction.

TABLE 6. OXYGEN IN WAH CHANG TANTALUM
USING A BATH OF Pt:Ta = 4:1

Oxygen, ppm	$(X - \bar{X})$	$(X - \bar{X})^2$
105 ± 3	2	4
99	-4	16
103	0	0
102	-1	1
106	3	9
104	1	1
100	-3	9
107	4	16
$\bar{X} = 103$	$\Sigma = 1$	$\Sigma = 56$

Note: Standard deviation = 2.8 ppm
Coefficient of variation = 2.7 per cent.

In view of the excellent oxygen results obtained on columbium by the platinum-bath method with a Pt:Cb ratio of 1:1, similar runs were made on tantalum. The extraction was made on 2-g samples at 1900 C for a minimum of 20 min. Platinum equal in weight to the following sample was dropped and degassed before dropping the sample. Three samples (nominal oxygen, 103 ppm) analyzed 72, 81, and 102 ppm. The first sample did not melt, perhaps because of poor contact with the small value of platinum. It melted with the next addition of platinum. The second and third samples melted on dropping. The cause of the low second result is believed to be the short (20 min) extraction time. A 30-min extraction of the third sample yielded the correct value. It appears that the longer time is required for complete extraction.

Another series of analyses was made using the same relative weights of platinum and tantalum. However, all the platinum was melted first and degassed. The Pt:Ta ratio was 0:1 for first sample and about 1:1 for the last sample. The results are listed in Table 7.

TABLE 7. OXYGEN IN TANTALUM
USING A BATH OF
Pt:Ta = 6:1 to 1:1

Sample(a)	Oxygen, ppm
28B	94
29A	122
29B	100
30A	104
30B	99

Note: Average = 104

Standard deviation = 10.8 ppm

Coefficient of variation = 10.4 per cent.

(a) The number indicates the disk, A and B the halves.

The standard deviation is only slightly higher than that for the larger columbium series at Pt:Cb = 1:1 (see Table 2) but the coefficient of variation is twice as high because of the difference in oxygen level. It is concluded that samples of either columbium or tantalum may be added to a platinum bath until the Pt:M ratio is reduced to 1:1 without measurably affecting the oxygen analyses.

Diffusion-Extraction Technique

The 3-ft length of 1/2-in.-diameter high-purity double arc-melted tantalum rod received from the Wah Chang Corporation and certified to contain <50 ppm oxygen was checked for oxygen homogeneity. Results by diffusion extraction at 2000 C ranged from 74 to 126 ppm. Hydrogen was consistent at 3 ppm and nitrogen ranged from 8 to 18 ppm. That the nitrogen recovery was quite incomplete was shown by the platinum-bath study.

A series of six consecutive 2-g samples of tantalum rod analyzed by diffusion extraction at 2000 C for 30 min averaged 93 ppm oxygen with a standard deviation of 2.4 and a coefficient of variation of 2.6 per cent. The individual analyses appear in Table 8. These samples were taken adjacent to those previously analyzed by the platinum-bath technique. It is seen that both techniques show excellent reproducibility but that the diffusion extraction results average 10 ppm lower than those by the platinum bath. It was thought that a higher diffusion-extraction temperature may be required.

A study, therefore, was made of the effect of increasing the diffusion-extraction temperature for tantalum from 2000 to 2100 C. Results for five samples at 2100 C averaged 96 ppm with a standard deviation of 2.3 and a coefficient of variation of 2.4 per cent. It is apparent that the increase in temperature had an insignificant effect on the analytical results. A few analyses at 2200 C ranged from 66 to 76 ppm. Variation in the high blank correction necessary at this temperature may account in part for the low values.

TABLE 8. OXYGEN IN WAH CHANG
TANTALUM ROD BY
DIFFUSION EXTRACTION

Oxygen, ppm	$(X - \bar{X})$	$(X - \bar{X})^2$
94 \pm 3	1	1
94	1	1
94	1	1
89	-4	16
96	3	9
93	0	0
$\bar{X} = 93$	$\Sigma = 2$	$\Sigma = 28$

Note: Standard deviation = 2.4 ppm.

Coefficient of variation = 2.6 per cent.

Oxygen-Doping Experiments

In order to check the accuracy of the oxygen analyses of tantalum, doping experiments were designed in which volumetrically measured amounts of oxygen were reacted with individual samples of low-oxygen tantalum. Analyses reflecting the sum of the small base oxygen content plus the known addition would prove the accuracy of the analytical techniques used.

A small quantity of low-oxygen 50-mil tantalum sheet was obtained from existing stock at Battelle. Three samples averaged 7 ppm oxygen by the platinum-bath technique. These and subsequent analyses appear in Table 9. Additions of 30 ppm oxygen were made to each of six more 3-g samples. Also, two control samples were heated in vacuum in a Sieverts apparatus at 900 C for 2-1/2 hr. See Series A and B, Table 9. This simulated the heating conditions for the doped samples but omitted the gas addition. The control samples averaged 15 \pm 1 ppm oxygen by diffusion extraction at 2000 C. Samples of Series A and B with the gas addition averaged 41 ppm oxygen with a standard deviation of 7.1 and a coefficient of variation of 17.2 per cent. The discrepancy between the calculated value after gas addition and the analysis averaged minus 4 ppm. This points to possible low recovery by diffusion extraction at 2000 C. It was reasoned that the high coefficient of variation (17.2 per cent) of these results also might be connected with the diffusion-extraction method. Therefore Series C and D samples were prepared and analyzed by the platinum-bath technique. It is seen that the analyses of control samples were consistent regardless of analytical technique. The over-all average of 14 ppm plus the 30 ppm from measured gaseous addition yielded samples with a nominal oxygen composition of 44 ppm. The platinum-bath results showed the same range of values as the diffusion-extraction results. This pointed to error in the Sieverts apparatus measurements. Because the residual pressure after doping was negligible the sensitivity of the McLeod gage measurement of the oxygen addition was reviewed. A very conservative estimate at maximum error in gage readings would account for only a 1-ppm variation in oxygen content of the specimen.

TABLE 9. ANALYSES OF OXYGEN-DOPED TANTALUM

Sample	Method	Oxygen, ppm
Base	Platinum bath, 1900 C	8
	Ditto	6
	"	7
<u>Series A</u>		
Control	Diffusion extraction, 2000 C	16
Doped	Ditto	45
	"	43
	"	33
<u>Series B</u>		
Control	Diffusion extraction, 2000 C	14
Doped	Ditto	51
	"	34
	"	37
<u>Series C</u>		
Control	Platinum bath, 1900 C	14
Doped	Ditto	56
	"	34
	"	41
<u>Series D</u>		
Control	Platinum bath, 1900 C	14
		36
Doped	Ditto	47
	"	37
	"	

An examination was made of the technique used in the doping of tantalum with oxygen which resulted in the erratic results just described. A temperature of 900 C had been used in the doping of this material with 30 ppm oxygen. A nonproject study made recently at Battelle on the reaction of tantalum and oxygen showed no change in the rate of reaction with oxygen as the temperature was increased from 600 to 800 C. Increasing the temperature to 900 C changed the rate only slightly. Therefore, it was decided to dope the samples at 600 C instead of 900 C to determine if more consistent results could be obtained. The results were as shown in Table 10.

TABLE 10. ANALYSES OF TANTALUM OXYGEN-DOPED BY IMPROVED TECHNIQUE

Sample	Method	Oxygen, ppm
Control	Diffusion extraction, 2000 C	7
Doped	Ditto	35
	"	39
	"	35
	"	42
Average		37.8
Nominal concentration		37

It is seen that a marked improvement in the reproducibility of analyses resulted when the tantalum was doped at the lower temperature. Two additional groups of tantalum samples were doped with about 30 ppm oxygen. For the first group, the sample first was degassed at 600 C for 1-1/2 hr. Tank oxygen dried by a Dry Ice-acetone trap was isolated in the calibrated volume of a McLeod gage. With the degassed sample at 600 C, the oxygen was expanded into the reaction tube of the Sieverts apparatus. Only a negligible pressure of gas remained at the end of 1 hr and the sample was cooled and removed for analyses.

It is seen (Table 11) that the average of the two control samples of this series is 15 ppm oxygen. Since the nominal composition of the individual samples varied, the deviation of the analyses is given. These range from -14 to +16 relative per cent. This is poorer agreement than reported in Table 10 and necessitates using the earlier high value for the control sample.

For the second group, the volume of the reaction section of the micro-Sieverts apparatus used in this work was reduced and five stopcocks were eliminated from the main reaction section. The sample degassing period was shortened from 1-1/2 hr to 5 min in order to lessen the chance of sample contamination during degassing. The results for this group of samples are also given in Table 11.

This set of results is perfect but of course is too brief to be statistically reliable.

TABLE 11. ADDITIONAL OXYGEN-DOPED TANTALUM SAMPLES

Sample	Oxygen, ppm		Deviation, relative per cent
	Added	Analyzed(a)	
<u>First Group</u>			
Control (before)	--	16	
Doped	30	40	-11
	28	50	+16
	28	43	0
	27	36	-14
Control (after)	--	14	
		Analysis avg	42
		Nominal avg	43
<u>Second Group</u>			
Doped	29	35	
	29	35	
Control	--	6	
<u>Third Group</u>			
Control (before)	--	7.7	
Doped	29.6	35	
	29.0	34	
	29.5	33	
Control (after)	--	7.2	

(a) By diffusion extraction at 2000 C.

A third group of tantalum sheet samples oxygen doped in the same manner were analyzed by the same technique, diffusion extraction at 2000 C. Two control samples were prepared, one before and one after the series of dopings.

It is seen that there was no detectable pickup of oxygen by the control sample. The analyses average 3 ppm or about 10 per cent low. This indicates that the accuracy is at least this good. Since the data show a negative bias, the error may be due to the diffusion-extraction technique and not the doping process. It is tentatively concluded upon the basis of the limited data in Table 11 that the accuracy of the diffusion-extraction technique for oxygen in tantalum at the 38-ppm level is quite reasonable and is of the order of ± 10 relative per cent.

When further low-oxygen tantalum is obtainable, a similar evaluation of the platinum-bath technique for tantalum should be made and the question of negative bias of the diffusion-extraction technique resolved.

Molybdenum

Iron-Bath Technique

A 20-ft length of low-oxygen molybdenum rod (1/4 in.) was purchased. Six spot-check samples over the entire length analyzed from 1 to 4 ppm oxygen for an average of 3 ppm. The analyses shown in Table 12 were made with an iron bath at 1650 C and a 20-min extraction. The molybdenum content was limited to 30 weight per cent of the melt. A series of five 5-g samples taken consecutively from one location in the rod gave an average oxygen analysis of 2.3 ppm with a standard deviation of 0.4 and a coefficient of variation of 17 per cent. These results also appear in Table 12. This is quite excellent reproducibility since the sensitivity of measurement of this level of oxygen in the apparatus is conservatively stated as equivalent to about 50 per cent. This very-low-oxygen molybdenum seemed to be a satisfactory base material for doping experiments. However, some difficulty in making oxygen additions was anticipated because of the volatility of MoO_3 .

TABLE 12. OXYGEN IN MOLYBDENUM ROD USING AN IRON BATH

Random Samples			Consecutive Samples		
Oxygen, ppm	$(X - \bar{X})$	$(X - \bar{X})^2$	Oxygen, ppm	$(X - \bar{X})$	$(X - \bar{X})^2$
4 ± 1	1	1	3 ± 1	0.8	0.64
1	-2	4	2	-0.2	0.04
3	0	0	2	-0.2	0.04
2	-1	1	2	-0.2	0.04
4	1	1	2	-0.2	0.04
4	1	1	$\bar{X} = 2.2$	$\Sigma = 0$	$\Sigma = 0.80$
$\bar{X} = 3.0$	$\Sigma = 0$	$\Sigma = 8$			

Note: For random samples

Standard deviation = 1.3 ppm

Coefficient of variation = 42 per cent

For consecutive samples

Standard deviation = 0.4 ppm

Coefficient of variation = 18 per cent.

Platinum-Bath Technique

A series of four 1.5-g samples of molybdenum rod (nominal 2.3 ppm oxygen) was analyzed for oxygen with a platinum bath at 2000 C for 30 min. The Pt:Mo ratio ranged from 30:1 to 10:1. The minimum ratio and extraction temperature were based on the molybdenum-platinum phase diagram (see the Appendix). The results were 3.5, 4.8, 5.2, and 6.2 ppm oxygen for an average of 4.9 ppm. These values are of the same order as those obtained with the iron bath but enough higher to raise the question of accuracy. Only further study could determine if the extraction is more complete with the platinum bath and which technique is more accurate.

Oxygen-Doping Experiments

Two samples of molybdenum with a base analysis of 2 to 4 ppm oxygen were doped with 12 and 30 ppm oxygen at 550 C. Analyses by iron bath at 1650 C showed 11 and 23 ppm respectively. The sample appeared to dissolve without difficulty. At this time, further doping experiments with molybdenum were postponed in favor of similar work on tantalum.

Tungsten

Iron-Bath Technique

Two 1/8-in.-diameter zone-purified tungsten wires were furnished by Mr. Judson Graab of NASA at Lewis Flight Center. These were analyzed by the iron-bath technique with the results shown in Table 13. The technique labeled "pressure drop" is the normal fractional freezing technique where the gases are frozen out one after the other. The expansion technique is to freeze out all gases but nitrogen which is pumped out and to expand the CO₂ while retaining H₂O as ice. The results on 2-g samples by expansion and 0.2-g samples by pressure drop were comparable. However, results on 0.2-g samples by expansion were 2 to 3 times as high. The limited precision or fluctuations in the rather high blanks do not explain the discrepancy. It would be of interest to determine if this represents a weakness in the expansion technique or an apparatus "peculiarity".

Platinum-Bath Technique

Before finding the W-Pt phase diagram (see Appendix) a series of four 0.3-g tungsten (NASA) samples were analyzed in a platinum bath at 1900 C for 20 min. The Pt:W ratio ranged from 12:1 to 3:1. The results were 3.6, 3.9, 2.8, 4.1 ppm oxygen which agree well with the previous iron-bath results. However, examination of the ingot showed that two samples, presumed to be the last, had not melted. Three other larger (2 g) samples analyzed with a constant Pt:W ratio of 4:1 yielded 3.1, 3.0, and 3.3 ppm oxygen. Extraction appeared complete in 10 min. Large unmelted portions of each sample were found imbedded in the ingot.

After finding the W-Pt phase diagram, three 0.4-g samples were set up with the Pt:W ratio to range from 26:1 to 10:1 dropping all platinum initially. As guided by the diagram, the temperature was raised to 2000 C; the extraction time was kept at 20 minutes. The results were 14, 14, and 17 ppm oxygen or about 2 to 3 times previous results. Whether this was due to the higher temperature is not known. The ingot showed two incompletely dissolved samples fused in its top.

These results are fragmentary but it seems clear that application of the platinum bath to tungsten will be difficult. The need for a high ratio of Pt:W and a temperature of about 2000 C is indicated. Since most of the samples dropped into the platinum baths did not melt, the gas was actually evolved as in the diffusion-extraction technique. The bath probably acted as a hindrance rather than a help. The results are almost sufficient

TABLE 13. OXYGEN IN ZONE-PURIFIED
TUNGSTEN USING AN IRON
BATH

Maximum Tungsten in Bath = 30 Per Cent;
Bath Temperature = 1650 C;
Extraction Time = 20-30 Min

Technique	Oxygen, ppm
<u>2-G Samples^(a)</u>	
Expansion	3.5
Expansion	4.0
Expansion	4.1
<u>0.2 to 0.3-G Samples^(b)</u>	
Pressure drop	5
Pressure drop	6
Expansion	11
Expansion	11
Expansion	14
Expansion	11
Expansion	18

(a) Precision = 0.2 ppm
Blank = 42 per cent of total.

(b) Precision = 2 to 1 ppm
Blank = 75 per cent of total.

to condemn the platinum-bath technique for tungsten. Some confirmation of the diffusion-extraction method is needed. If it should prove satisfactory, then, the choice of methods for determining oxygen in tungsten would appear to be between it and the iron bath.

APPARATUS AND COMPONENT DESIGN AND OPERATION

Recently, there has been much activity in devising other techniques than the usual fractional freezing or dry chemical absorption of the low-pressure gas for analyzing the gases evolved in vacuum-fusion analysis. Because of their newness or limited employment the alternate techniques have not been scrutinized by enough analysts to confirm their validity or point out their weaknesses. Therefore, two such techniques were evaluated as part of this investigation. These are the use of a Hopcalite-Ascarite mixture for fast absorption of carbon monoxide and the substitution of the entire analytical train by a chromatograph.

HOPCALITE-ASCARITE ABSORBENT

A Hopcalite-Ascarite mixture has been used by Covington and Bennett⁽⁴⁾ for the rapid determination of oxygen in titanium. This absorbent is also used in a commercial apparatus of the Covington design manufactured by the Laboratory Equipment Corporation. It appeared of value to evaluate the absorbent for speed and completeness of pickup of CO and for possible interference by unwanted pickup of hydrogen.

The performance of two lots of Hopcalite used in rapid vacuum-fusion analysis was examined. One lot was from the Laboratory Equipment Corporation (LECO) and the other from Mine Safety Appliances Company (MSA). Mixtures of 25 g of Hopcalite and 25 g of Ascarite were inserted in a micro-Sieverts apparatus and operated at room temperature. Gas additions to the apparatus were metered roughly from a gas buret and measured exactly with a McLeod gage in the calibrated system.

When 1-ml additions of CO were admitted to the LECO Hopcalite mixture 96 per cent was absorbed in 5 sec and 99 per cent in 5 min. Little or no further pickup was observed at the end of 15 min. With smaller additions of 0.25 ml, 90 per cent was absorbed in 5 sec and 99 per cent in 5 min. The MSA Hopcalite had a slower initial reaction. Only 80 per cent of 1 ml and 63 per cent of 0.25 ml of CO was absorbed in 5 sec. In both cases, absorption was about 99.5 per cent complete in 5 min. Thus it was demonstrated that the Hopcalite-Ascarite mixture is a means of rapid and complete (from a practical standpoint) absorption of CO.

However, two tests made with 1-ml additions of hydrogen showed a possible absorption of about 10 per cent in 15 min by LECO Hopcalite plus Ascarite. Two 0.25-ml additions showed a 30 per cent absorption in one case and nil in the other. Because, in the analysis of titanium, the absorbed gas is assumed to be all CO, simultaneous absorption of hydrogen might invalidate the results. Therefore, the extent of this interference was evaluated. The experimental data for LECO Hopcalite are given in Table 14. Hydrogen volume additions of about 0.25 and 1.00 ml STP were made. Measurable absorption occurred in as little as 5 sec and increased with time. The trend was confirmed by readings of 23 per cent absorption after 75 min and 94 per cent absorption overnight. In contrast, helium showed the same absorption in 24 hr as hydrogen did in 5 sec (about 2 or 3 per cent). Only minor corrections were required for the long-time virtual leak rate of the apparatus.

To put the data on a meaningful basis an absorption time of 5 min and a sample (titanium) weight of 0.25 g was assumed. To yield 0.25 ml of hydrogen the sample would analyze 90 ppm (1.0 ml = 360 ppm) which is a high but not unusual hydrogen content. Assuming a typical 5 per cent or 0.0125-ml absorption of hydrogen calculated as CO, the oxygen value would be high by 36 ppm. This discrepancy probably would not be considered important in routine control analysis, particularly if the hydrogen content was lower than the 90 ppm of the example. However, where an exact measurement of oxygen content of titanium is required it would seem best to avoid the Hopcalite-Ascarite mixture.

(4) L. C. Covington and S. J. Bennett, Analytical Chemistry, 32, 1334-1337 (1960).

TABLE 14. HYDROGEN ABSORPTION BY A
HOPCALITE-ASCARITE MIXTURE

Added, ml STP	Residue, ml STP, After Indicated Time			Volume Per Cent Remaining After Indicated Time		
	5 Sec	5 Min	15 Min	5 Sec	5 Min	15 Min
1.02	0.986	0.967	0.933	96.7	94.8	91.5
1.00	0.979	0.956	0.925	97.9	95.6	92.5
1.00(a)	0.964	0.945	0.915	96.4	94.5	91.5
1.12(b)	1.05	1.03	0.996	93.8	92.0	88.9
0.25	0.247	0.241	0.233	98.8	96.4	93.2
0.28	0.256	0.248	0.240	91.4	88.6	85.7

(a) After 75 min 0.772 ml or 77.2 per cent remained.

(b) After 1060 min .0621 ml or 5.54 per cent remained; using helium (1.05 ml), 97.3 per cent remained after 1480 min. Long-time blanks equaled 0.0157 ml hydrogen per 1000 min.

In analysis for oxygen in columbium or tantalum, the sample size would usually be higher by a factor of 10 and the discrepancy correspondingly lower. Thus, the discrepancy for these metals would not be significant except for samples containing about 30 ppm oxygen which was associated with greater than 10 ppm hydrogen.

CHROMATOGRAPH

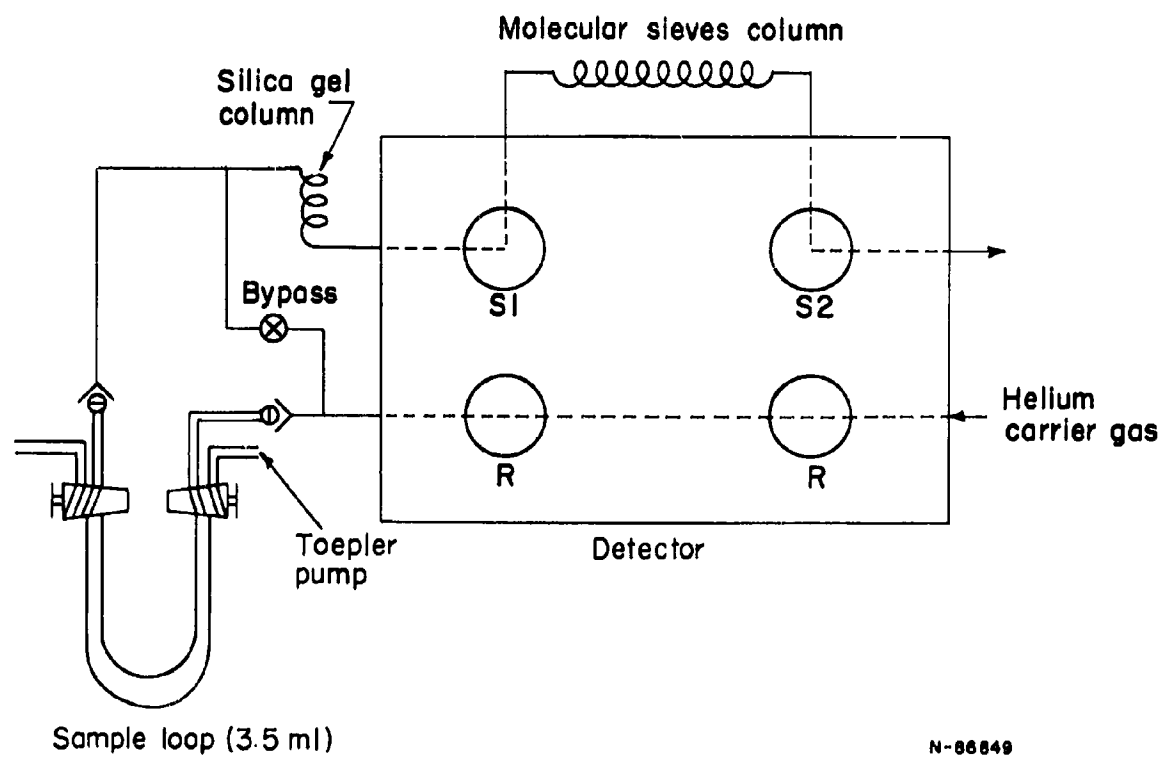
An exploratory experiment at Battelle 2 years ago indicated the feasibility of analyzing by gas chromatograph for quantity and type of gas mixture evolved in vacuum-fusion analysis. Since then, successful application of the chromatograph to vacuum fusion has been reported by Dr. A. J. Frank at Denver Research Institute(5), by Dr. H. Feichtinger of the Georg Fischer Company, Schaffhausen, Switzerland(6), and by the W. C. Heraeus, GMBH, Hanau, West Germany(7), in their vacuum fusion analyzer VII-6. At the recent meeting of the ASTM committee on oxygen in columbium in Pittsburgh, Dr. Velmar A. Fassel reported a similar application of the chromatograph to gases evolved by arcing a sample in an inert gas atmosphere. Because one of the goals of this study was to make recommendations for redesign of vacuum-fusion apparatus, an exploratory test was started on the use of a combination of vacuum-fusion and chromatographic equipment.

Gas-Chromatography Equipment

The gas chromatography was done with a dual-column, dual-detector instrument. The essential components of the chromatograph are shown in Figure 1. After the helium

(5) A. J. Frank and J. J. E. Schmidt, "Analysis of Gases in Metals", Progress Reports: No. 1, 8/1/59, No. 2, 11/6/59, and No. 3, 2/3/60. Contract AF 33(616)-6381, Project No. 9-(8-7360). Task No. 73609, Denver Research Institute.

(6, 7) Commercial literature.



N-66649

FIGURE 1. GAS CHROMATOGRAPH

carrier gas passes the two reference detector filaments, R, it may be made to follow one of two paths.

- (1) With the stopcocks on the sample loop closed and the bypass valve open, the carrier gas enters the silica gel column without entering the sample loop.
- (2) With the three-way stopcocks properly adjusted, and the bypass valve closed, the carrier gas flushes the content of the sample loop into the silica gel column.

The silica gel column retains carbon dioxide for a short period of time but permits hydrogen, oxygen, nitrogen, methane, and carbon monoxide to pass Detector S₁ and be recorded as a composite peak on the chromatograph. As these gases enter the molecular sieves column, the carbon dioxide is eluted from the silica gel column and is recorded as it passes over Detector S₁. The gases from the molecular sieves column are eluted in the following order: hydrogen, oxygen, nitrogen, methane, and carbon monoxide and are recorded by means of Detector S₂. The carbon dioxide remains on the molecular sieves column.

Sampling Procedure

The gas-chromatography sample loop becomes an integral part of the vacuum-fusion apparatus when the one stopcock is closed and the other stopcock is set to connect the Toepler pump and the gas sample loop. The gas sample loop is evacuated with the vacuum-fusion equipment. See Figure 2.

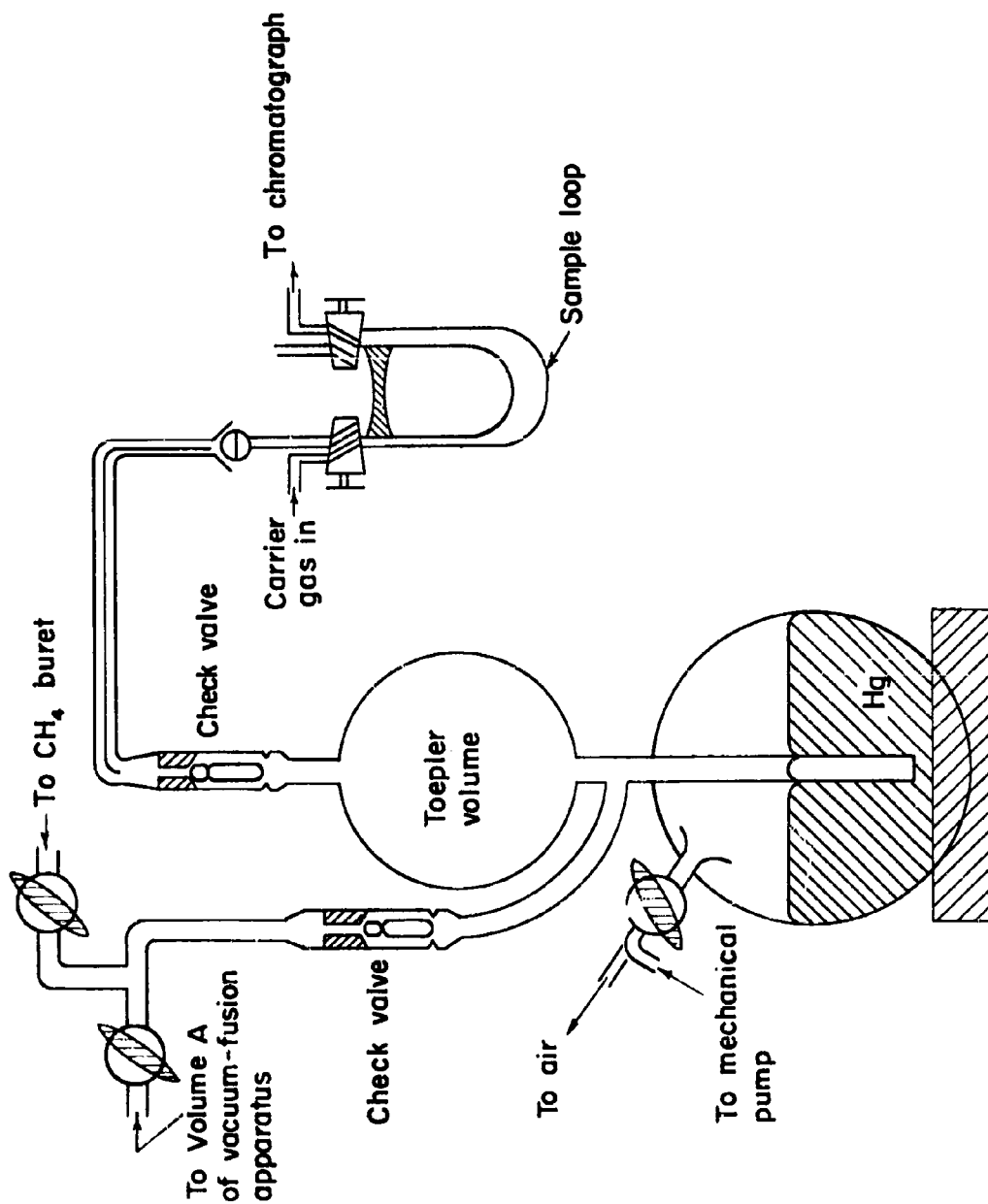
Gases from the vacuum-fusion furnace were collected in Volume A which includes a McLeod gage and the pressure was recorded. These gases are then expanded into Volume B which contains the Toepler pump and sample loop. The gases in the Toepler pump were then compressed in the gas-chromatography sample loop using a single stroke. Approximately half the gases collected were used for gas-chromatography analysis and the other half remained in Volume A for comparative results by the conventional vacuum-fusion method.

Internal-Standard Method

To help interpret the chromatographic data, it was decided to add an internal standard to the gas sample. The internal-standard method of analysis, when applied to gas chromatography, requires the quantitative addition of a known amount of reference gas to the sample. The reference gas must have an elution time near that of the sample gases.

The peak area obtained for the known quantity of internal standard can then be quantitatively related to the peak areas of the sample components. A correction factor must be applied to each gas because each one has a different sensitivity to the detector due to the differences in thermal conductivity.

Methane was chosen as the internal standard in this work. A known amount of methane was added to the gas in Volume A before the gas sample was transferred from



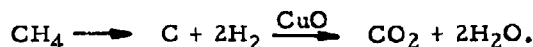
N-66850

FIGURE 2. VACUUM-FUSION CHROMATOGRAPHIC SAMPLER

the furnace to Volume A. The amount of methane in the total sample can be calculated and used for the quantitative determination of each gas in the sample.

Initial Experimental Results

It was shown that for the proposed comparison of usual vacuum-fusion gas separation and identification the methane standard must be introduced only to the portion of the gas sample going to the chromatograph. A sample of methane passed over the hot CuO in the usual manner for vacuum-fusion analysis showed a drop in pressure in passing through the liquid-nitrogen cold trap. It was assumed that the methane was cracked and oxidized according to the following equation



Since the Dry Ice-acetone removed the H₂O as it was formed and 1 mole of CO₂ replaced 1 mole of CH₄, no net change in pressure resulted until the liquid nitrogen was applied. About 8 per cent of the CH₄ underwent this reaction in 30 min.

The sensitivity for the gas-chromatography method using approximately one-half the gas from the furnace and a 1-g sample was about 0.08 ppm oxygen as carbon monoxide or 0.15 ppm oxygen as oxygen, 0.15 ppm nitrogen, and 0.5 ppm hydrogen. The sensitivity of the hydrogen measurement could be greatly improved by using argon instead of helium as the carrier gas. Complete resolution of the gases and sharp narrow peaks were obtained in this study.

Improved Procedure and Results

The method of introducing the internal standard (methane) was changed because of the reaction of CH₄ with CuO. A combination manometer-buret was introduced directly between Volume A and the Toepler pump. See Figure 2. The buret had an independent vacuum system and a connection to a lecture bottle of methane. The methane was stored in the buret until it was ready to be mixed with the sample gas.

The leads from the gas-chromatography sample loop to the instrument were shortened and smaller-diameter tubing installed. Less tailing off of the sample in the carrier gas resulted, giving sharper chromatograms.

Sample Analysis

A sample of 3/8-in. carbon steel drill rod was analyzed by low-pressure fractional analysis (L-PFA) and gas-phase chromatography (GPC). The gas from the vacuum-fusion furnace was divided; approximately one-half of the sample gas was mixed with the internal standard and the other half was analyzed by the L-PFA method without methane present.

The results of five determinations are shown in Table 15.

TABLE 15. COMPARISON OF RESULTS BY GAS CHROMATOGRAPHY
AND LOW-PRESSURE ANALYSIS

Drill Rod	Oxygen from CO, ppm		Nitrogen, ppm	
	L-PFA	GPC	L-PFA	GPC
2	16.0	17.6	20.2	19.1
4	19.8	17.4	15.2	11.6
3	20.7	20.2	21.6	23.2
5	20.5	18.9	14.5	13.0
6	18.2	20.4	16.4	16.4
Avg deviation, ppm		1.7		1.6
Max deviation, ppm		2.4		3.6

Discussion of Results

The differences between the two methods show random variations for both the oxygen and nitrogen results which are within the accuracy of the methods, except for the nitrogen result for Drill Rod 4. The attenuation was not properly adjusted when Drill Rod 4 sample gas was chromatographed. The improper attenuation adjustment necessitated a different method of calculating the relative amounts of carbon monoxide and nitrogen present relative to the amount of internal standard present. The difference in the calculating method is more fully explained in the next section. However, an improper attenuation will cause less accurate results regardless of the method used for calculating.

Calculation of Results

Of the sample gas from the vacuum-fusion furnace quantitatively divided into two fractions, the known quantity for the gas-chromatography analyses was expanded into the Toepler pump to which had been added the internal standard. A pressure reading on the new calibrated total volume of the mixture permitted the calculation of the exact volume of internal standard added.

Other details of operation of the chromatographic system remained as described earlier. A reproduction of a chromatogram taken from one of the samples analyzed is shown in Figure 3. The first peak is the composite peak which represents all gases which might be present, except carbon dioxide, passing through the first detector. The composite peak is not used in the analyses. The succeeding peaks represent nitrogen, methane, and carbon monoxide, respectively. A disk-type integrator was used to determine the relative amount of each gas present. As the recorder pen moves up scale, the integrator pen increases its rate of movement providing a quantitative relation for the various gases present. The integrator counts are shown at the bottom of the chromatograph. If a peak is attenuated to keep it on scale, the integrator counts are multiplied by the attenuator factor. Such factors appear in Figure 3.

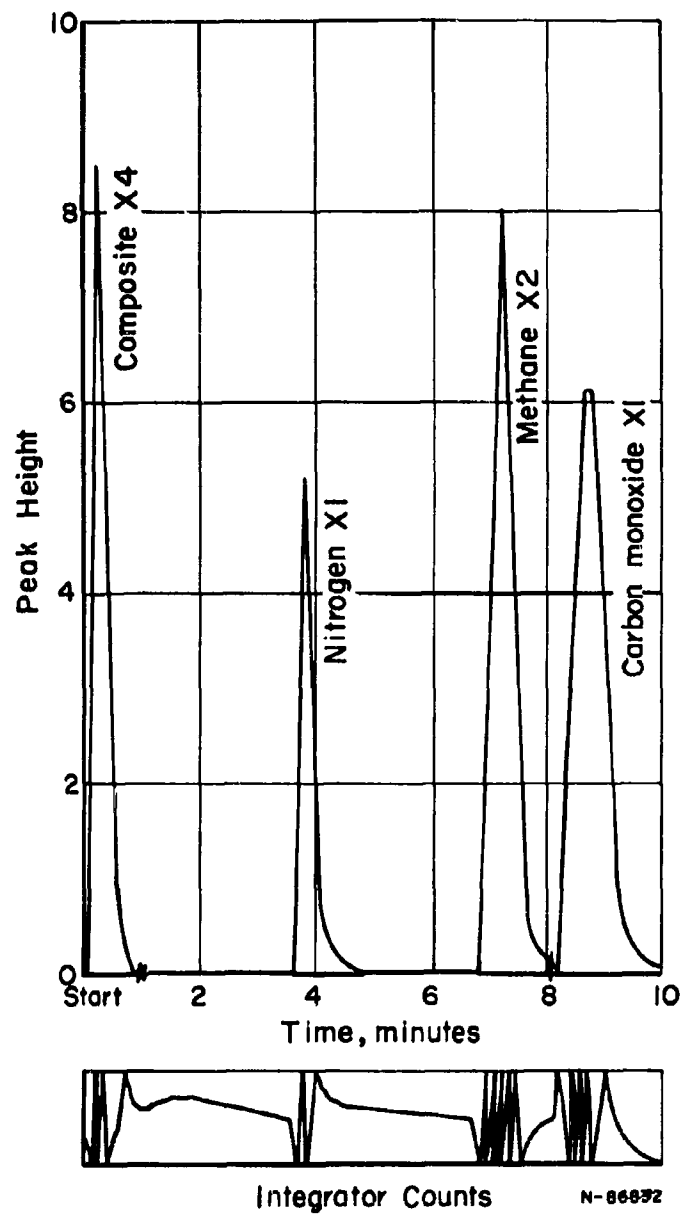


FIGURE 3. TYPE OF CHROMATOGRAM FOR STEEL

The milliliters of internal standard (methane) in the sample-methane mixture were known, therefore, the number of integrator counts per milliliter of methane could be calculated. The milliliters of carbon monoxide and nitrogen were then calculated by relating the integrator counts for each of these gases to the counts per milliliter of methane, and correcting the nitrogen and carbon monoxide for differences in detector sensitivity due to the thermal conductivity of the various gases. The milliliters of carbon monoxide and nitrogen were multiplied by the factor required to account for the portion of gas reserved for low-pressure fractional analyses. The calculation for Drill Rod 4 was done in the same manner, except that peak areas were used instead of integrator counts. The calculation from the point where the gas volumes were known was the same as used for the data from the low-pressure fractional analyses.

Correction Factors

Quantities of methane, carbon monoxide, and nitrogen were individually measured into a known volume of the vacuum-fusion apparatus in duplicate. The gases were collected through the Toepler pump and sample loop system and chromatographed. The sensitivity of each gas to the thermal conductivity detector was determined and correction factors calculated with methane assigned a value of 1.

The correction factors obtained from the duplicate analyses were 0.870 for carbon monoxide and 0.795 for nitrogen. Values obtained by calculating correction factors from thermal-conductivity data taken from the Handbook of Chemistry were 0.869 for carbon monoxide and 0.793 for nitrogen. It is seen that the agreement is excellent.

Conclusions and Suggestions

The gas-chromatography method using an internal standard showed promise as an alternative to the usual analytical train of the vacuum-fusion apparatus. However, additional determinations should be made on the same sample already analyzed five times to obtain sufficient data for reliable statistical evaluation. Also a series of samples of known gas mixture should be introduced to the vacuum-fusion apparatus and analyzed by both the chromatographic and low-pressure fractional methods. Such a mixture should be analyzed as samples are now and a sufficient number of runs made to determine statistical reliability for multiplicate analyses.

After firming up its reliability, the chromatographic technique should prove quite useful in exploration of vacuum-fusion gases for "odd" gases suspected by some investigators and theoreticians as possible constituents of the extracted gases. Of course, a different internal standard would be required for studies of methane evolution.

RECOMMENDATIONS FOR FURTHER WORK

1. In addition to studies on doped samples, validation of accuracy should be attempted by the newer technique of neutron activation analysis. The latter analyses may be provided by Battelle Memorial Institute or other organizations.
2. The use of a concentrator (Battelle proprietary), coupled with the induction coil, for heating samples under vacuum should be investigated. If useable this will obviate the graphite insulation which surrounds the graphite crucible and contributes to the blank.
3. Research on the use of gas chromatography should continue (1) for the comparison with conventional analytical systems and (2) as a source of information on the presence of unknown gases.
4. Because of their reported convenience and reliability in separating hydrogen from other gases palladium filters should be investigated.
5. Platinum-metal ratios should be evaluated further to determine the minimum ratio which will permit complete gas extraction.
6. Investigations should continue on the platinum-bath, iron-bath, and diffusion extraction techniques for the gas analysis of molybdenum and tungsten.
7. Investigation should continue on basic factors inherent to vacuum-fusion technique. For example, discrepancies have been observed, in analyzing small samples, between the techniques of (1) freezing out and re-expanding for CO measurement and (2) measurement of CO by pressure difference after freezing. The results did not differ when larger gas volumes were obtained from larger samples. A critical look should be taken at this anomaly, which may lead to serious error.

APPENDIX

PHASE DIAGRAMS PERTINENT TO THE VACUUM-FUSION ANALYSIS OF REFRACTORY METALS

Phase diagrams pertinent to the study are presented on the following pages. They were extracted from DMIC Report 152, April 28, 1961. See Figures 4, 5, 6, 7, 8, and 9. These are for the Mo-Pt, W-Pt, Cb-Fe, Ta-Fe, Mo-Fe, and W-Fe systems, respectively.

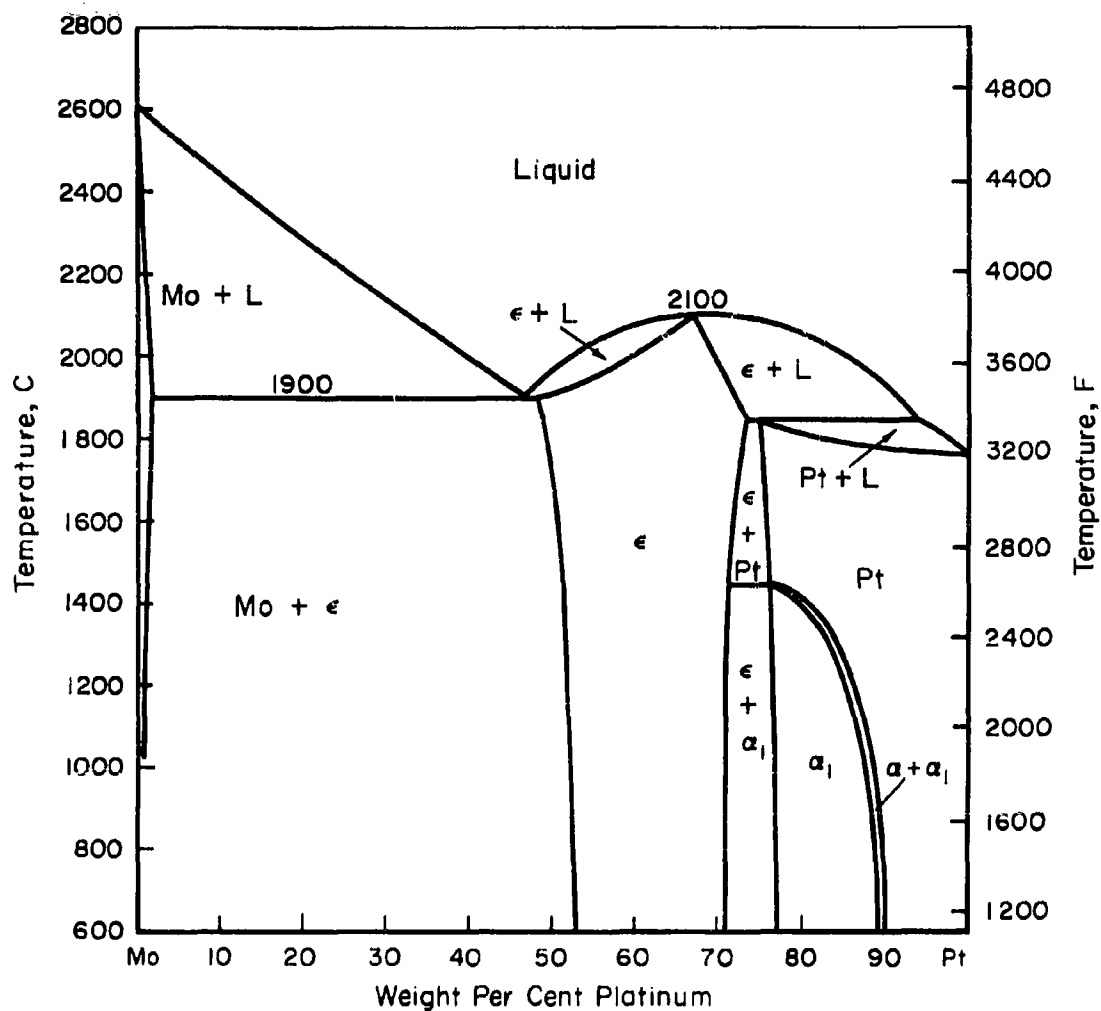


FIGURE 4. MOLYBDENUM-PLATINUM SYSTEM

Knapp verified Raub's findings of an intermediate phase ϵ with a hexagonal-close-packed structure, with $a = 2.80$ Å and $c/a = 1.603$, at the molybdenum side, and $a = 2.786$ Å and $c/a = 1.611$, at the platinum side. α_1 is face-centered tetragonal with $a = 3.895$ Å and $c/a = 1.005$ to 1.009. The solubility of platinum in molybdenum is very slight.

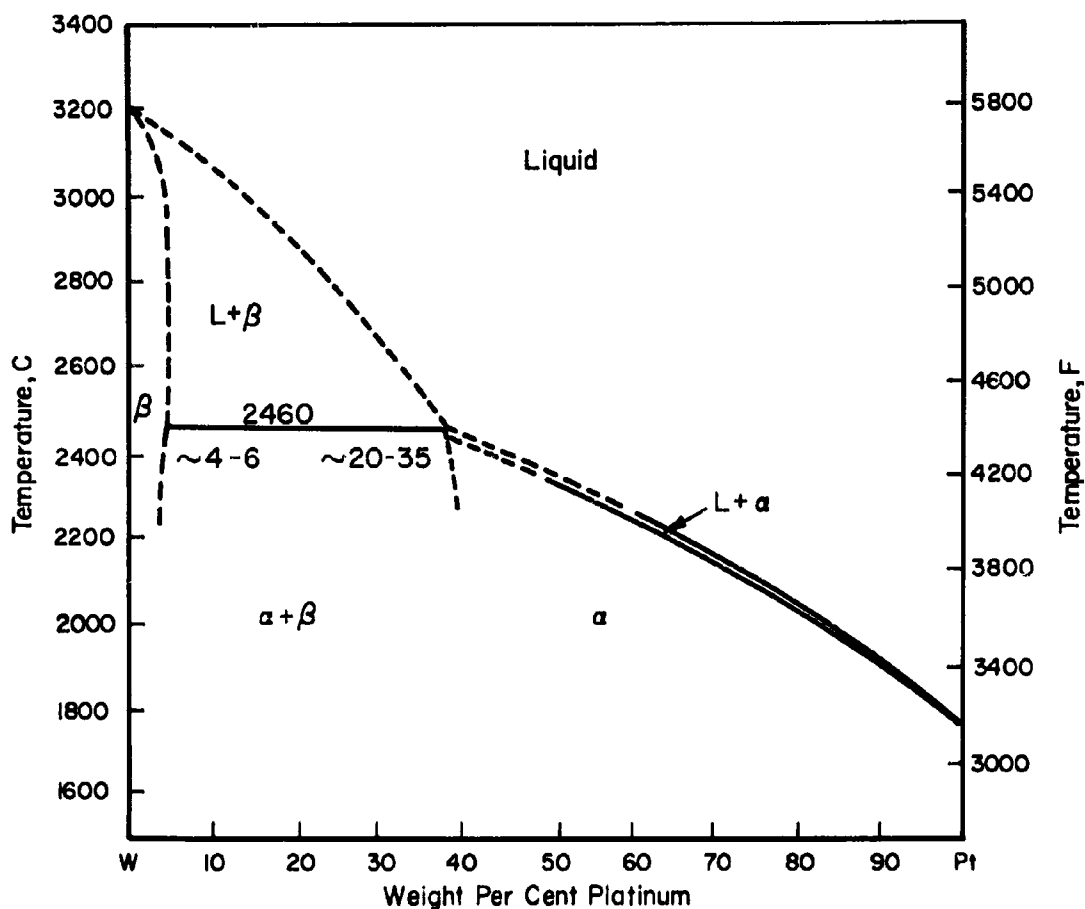


FIGURE 5. TUNGSTEN-PLATINUM SYSTEM

The maximum solubility of platinum in tungsten at the solidus temperature lies between 4 and 6 weight per cent platinum. Platinum and tungsten form a series of solid solutions up to a maximum of 62 weight per cent tungsten. Nemilov found evidence of an order-disorder transformation in the range of 75 atomic per cent tungsten (76 weight per cent).

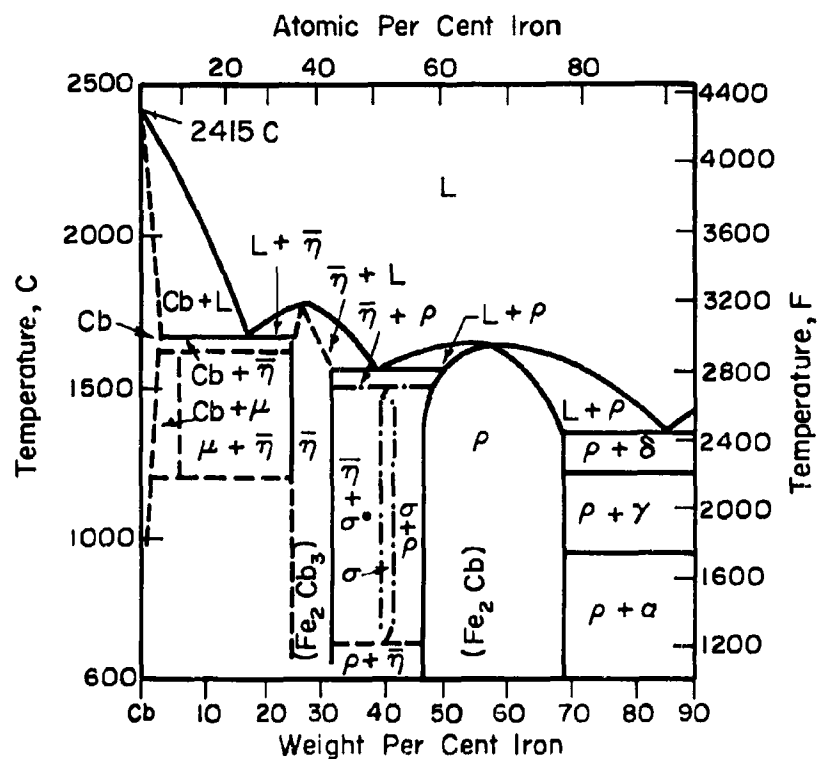


FIGURE 6. COLUMBIUM-IRON SYSTEM

The phase diagram prepared by Goldschmidt shows a high-temperature σ -phase similar to other transition-metal systems. Fe_2Cb_3 is an η -carbide-type structure with $a = 11.239 \text{ \AA}$. Fe_2Cb is isotypic with MgZn_2 with $a = 4.830 \text{ \AA}$, $c = 7.822 \text{ \AA}$, and $c/a = 1.632$. The terminal solid solutions of columbium in iron and of iron in columbium are small and decrease with decreasing temperature.

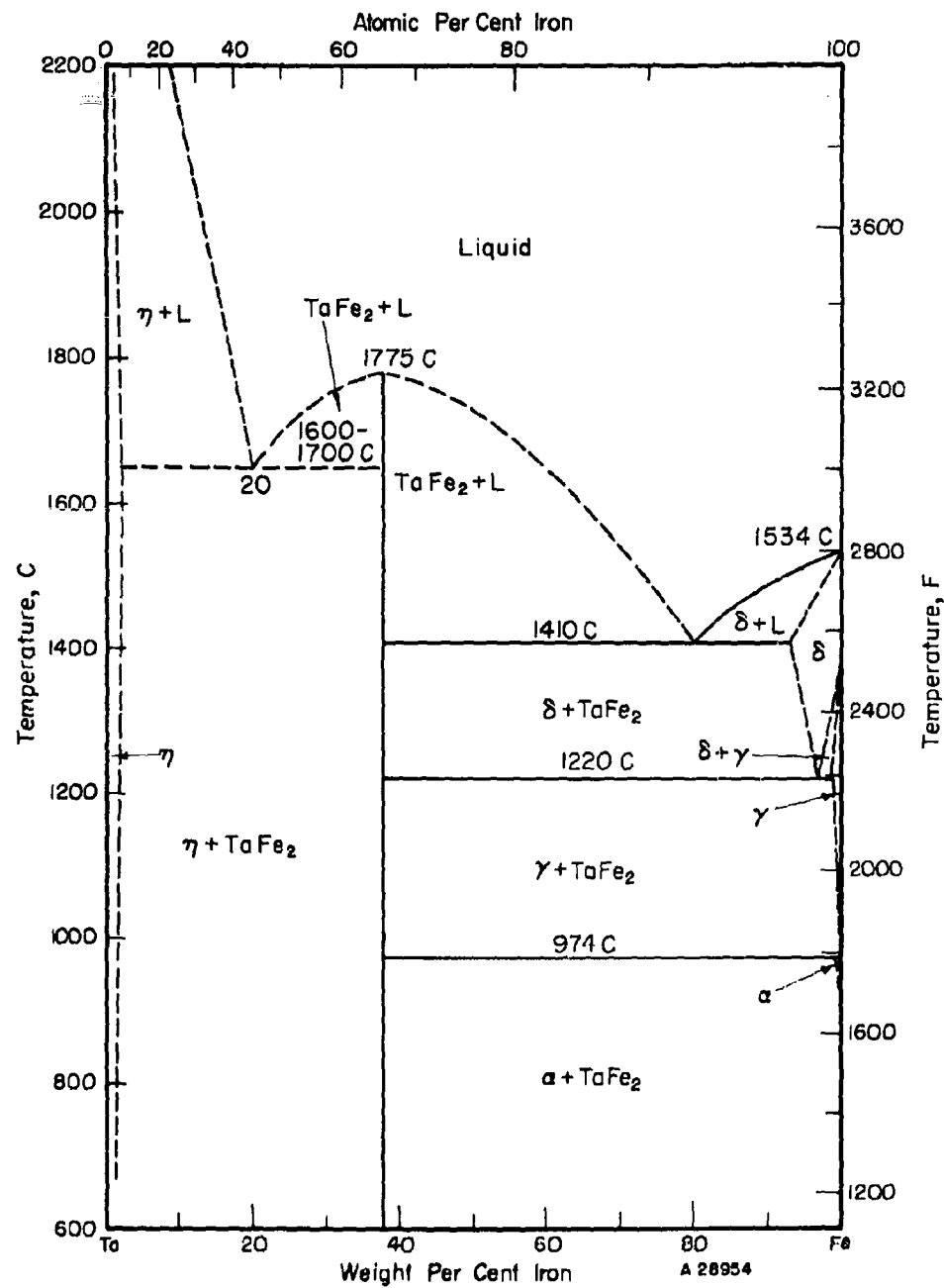


FIGURE 7. TANTALUM-IRON SYSTEM

TaFe₂ has the MgZn₂ (C14) type of structure with $a = 4.81 \text{ \AA}$, $c = 7.85 \text{ \AA}$, and $c/a = 1.83$. The diagram was developed by Genders and Harrison.

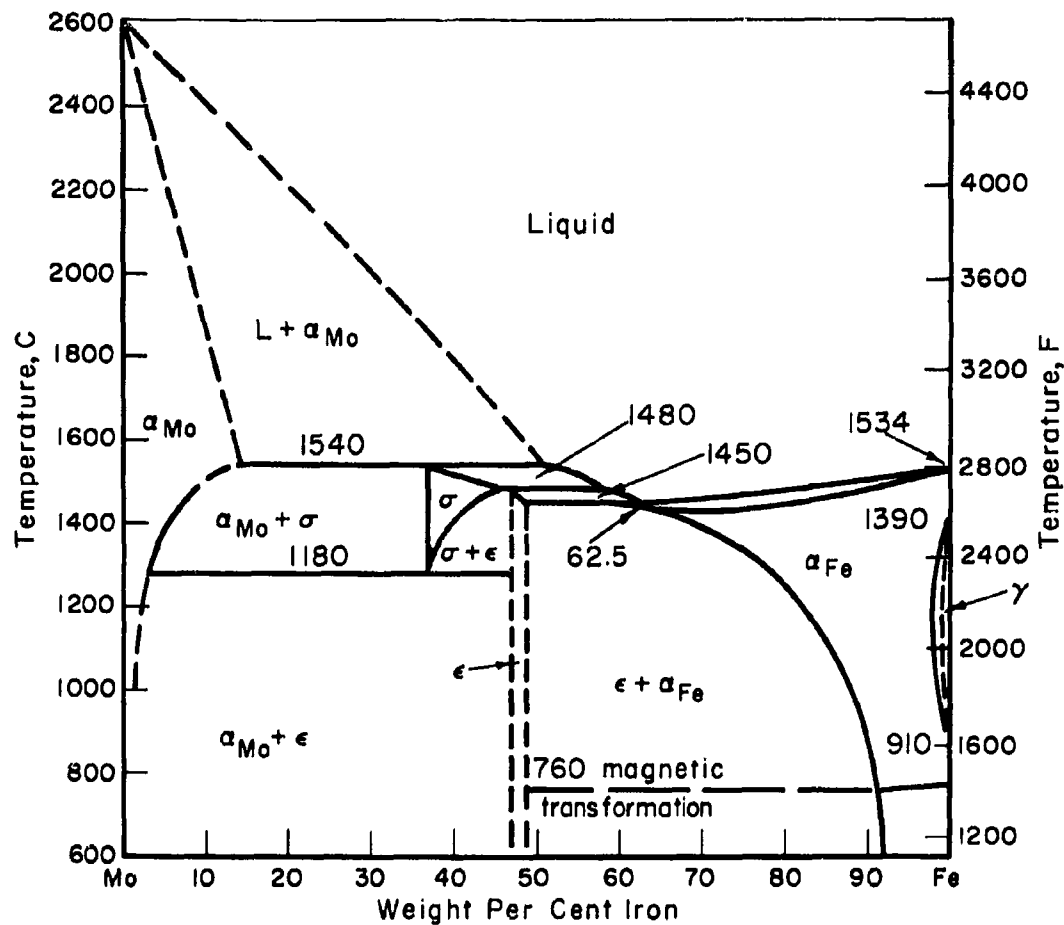


FIGURE 8. MOLYBDENUM-IRON SYSTEM

The ϵ -phase is rhombohedral of the W_6Fe_7 ($D8_6$) type, with $a = 8.99 \text{ \AA}$, $\alpha = 30^\circ 38.6'$. The structure of the α -phase is tetragonal, with $a = 0.188 \text{ \AA}$, $c = 4.812 \text{ \AA}$, and $c/a = 0.5237$ at 36 weight per cent iron (50 atomic per cent). There are 30 atoms per unit cell. The solubility of iron in molybdenum is 10.5, 6.7, 4.8, 3.6, and 2.7 weight per cent at 1480, 1400, 1300, 1200, and 1100 C, respectively.

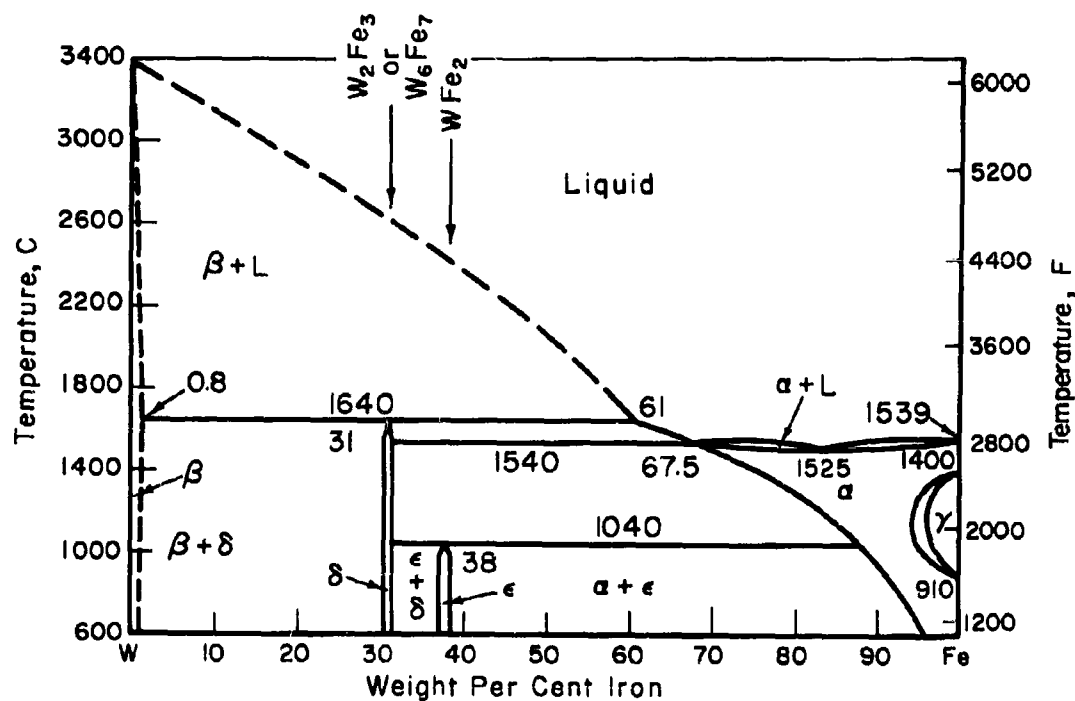


FIGURE 9. TUNGSTEN-IRON SYSTEM

WFe_2 is isomorphous with the hexagonal $MgZn_2$ (C14) structure, with $a = 4.735$ kX, $c = 7.706$ kX, $c/a = 1.627$. Sykes reports the δ -phase as W_2Fe_3 with $a = 4.731$ kX, $c = 26.76$ kX, and $c/a = 5.440$. The structure has trigonal Laue symmetry with 39 to 40 atoms per unit cell. Arnfelt reported the δ -phase as W_6Fe_7 (D8₅ type) with 13 atoms per unit cell. The structure is rhombohedral with $a = 0.04$ Å and $\alpha = 30^\circ 30.5'$. The solubility of iron in tungsten is 0.8 weight per cent at 1640 C with little change in solubility with temperature.

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